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ABSTRACT

Low-energy irradiation of degassed magnesium oxide powder produces paramagnetic centers. Electron paramagnetic resonance (e.p.r.) spectra for three types of surface centers were obtained by degassing over a range of temperatures. The first type which was found after irradiation following degassing through 300° and 400° C has a g value of 2.0031, the second after a 500° to 700° C degassing temperature has a g of 2.0001 (for the 600° C degassing temperature $g_{\perp} = 1.9998$ and $g_{\parallel} = 2.0012$), and the third type after a 800° to 900° C degassing temperature has a g value of 2.0005. The g values and the e.p.r. line shapes have been used to establish the structures of the defects. Comparison studies were also made using magnesium oxide doped with ferric iron, aluminum, and lithium cations.

INTRODUCTION

A more complete understanding of surface defects is now possible through the use of electron paramagnetic resonance (e.p.r.) techniques.[1-3] At least some of these defects are important in such surface phenomena as chemisorption, catalysis, sintering, diffusion, and dissolution. Many of the defects occur naturally in high surface area materials while others

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may be produced by irradiation.

This paper will deal primarily with point defects on high surface area magnesium oxide. Before irradiation, such defects as oxygen vacancies, magnesium vacancies, and aggregates of these apparently exist on the surface. When these vacancies are irradiated with ultraviolet light, they trap electrons, or holes, and become surface analogs of bulk color centers; F, V, M, etc. In previous papers, some of the irradiation-induced centers on MgO were shown to be effective in catalysis of the hydrogen-deuterium isotopic exchange reaction,[3] in chemisorption of CO_2 as CO_2^-,[4] and in chemisorption of O_2 as O_2^-.[2,5]

The purpose of the present work is to show the types of defects which exist on the surface of the unirradiated material, as well as to continue to explore some of the irradiation-induced centers that can be formed. The vacancies themselves are not paramagnetic; however, by studying the e.p.r. spectrum of the defect with the trapped hole or electron, one can deduce to some extent the type of defect that existed before the charge carrier was trapped. To minimize the possibility of creating lattice vacancies, ultraviolet light was used rather than X or γ radiation.

EXPERIMENTAL

The magnesium oxide used in this experiment was prepared from reagent grade powder.[6] The powder was boiled in distilled water for several hours, extruded into pellets with a hypodermic syringe, and dried in air at 100° C. The MgO hydrolyzed in the hot water to form $Mg(OH)_2$.

Samples with altervalent anions and cations were prepared by adding a known amount of impurity as a soluble salt to the slurry of water and MgO. By this method samples were doped with $FeCl_3$, $Fe(NO_3)_3$, and $AlCl_3$. Lithium was added to the slurry as the metal which rapidly reacted with the water to form LiOH. Most of the work was done on the undoped material (which contained 0.0015% Fe) and on the powder doped with $FeCl_3$ to a total iron content of 0.006% Fe (by weight). The former material is designated MgO sample I (MgO I) and the latter is MgO sample II (MgO II).

The MgO was irradiated at about 30° C by using a low-pressure mercury-vapor lamp with an intensity of 60 $\mu W/cm^2$ at 2537 Å. Best reproducibility was obtained when the samples were irradiated in a dynamic vacuum of less than 10^{-5} torr. A partial pressure of O_2 as low as 5×10^{-4} torr will rapidly destroy some of the spectral bands.

A conventional e.p.r. spectrometer operating at 9.3 Gc/sec and in the TE_{102} mode was employed. The magnetic field was monitored continuously by a nuclear magnetic resonance gaussmeter. The g values were obtained by comparison with the value for Cr^{+3} in MgO ($g = 1.9797$). When this line was not present in the sample's spectrum, it was introduced into the spectrum by taping a small single crystal of MgO (containing Cr^{+3}) onto the outside of the sample tube. The estimated error (from e.p.r. instrument to instrument) in g values is 0.0003; however, the relative error between the g values within this experiment is closer to 0.0001. Intensity measurements (spin concentrations) were made by comparing the integrated intensity of a line with a standard of pitch in KCl. The estimated error in the spin concentration is ±30%.

The basic experimental procedure consisted of slowly heating (degassing) a sample to the desired temperature (about 4 hours) while it was being evacuated. The sample was then held at that temperature and evacuation was continued until a pressure of 3×10^{-5} torr or better was obtained. This pressure was always obtained in less than 2 hours; therefore, a 2-hour standard annealing time was adopted. After each heating the sample was cooled to room temperature and an e.p.r. spectrum was determined. The sample was then UV-irradiated, and another spectrum was determined. This procedure was carried out first at 300° C, and then at 100° increments until 900° C was reached.

Surface area measurements of the degassed unirradiated MgO samples were made at -196° C using nitrogen as the absorbate.

RESULTS

Figure 1 shows the e.p.r. spectra produced by irradiation of the high-surface-area MgO II. The spectrum of three different centers, termed S_1, S_2 and S', appeared during the range of degassing temperatures.

The S_1 type center (Fig. 1(a)) was formed after degassing, or decomposing, the $Mg(OH)_2$ at 300° C followed by ultraviolet irradiation. After the 400° C degassing and irradiation, the shape of the center was somewhat altered and the derivative spectrum reached its maximum intensity. At degassing temperatures above 500° C only a weak S_1-center line appeared. The g value of this center, taken where the first derivative curve crosses the base line, is 2.0031.

The next center to form, as the MgO was heated to even higher temperatures, was the designated S_2 center. The spectrum of this

center, shown in Fig. 1(b), first appeared after the 500° C heating but was strongest after the 600° C degassing. The shape of the spectrum is typical of an unpaired electron in uniaxial symmetry. Lebedev[7] has calculated curves of such centers, and values of $g_{\perp} = 1.9998$ and $g_{\parallel} = 2.0012$, with an error of ± 0.0003, were determined by comparing the experimental curve with the calculated curves. In auxiliary experiments it was verified that the intensity of the S_2 center increased at a much greater rate than the other centers, and the amplitude of the line reached about half of its saturation intensity after approximately 3 minutes of irradiation. A much weaker line (Fig. 1(c)), also of the S_2 type, was formed when the sample, that had been degassed at 700° C, was irradiated.

After the 800° C heat treatment, a stronger line could be produced by irradiation; however, this line grew in intensity much more slowly than the 600° C spectrum, and it reached saturation only after 50 to 60 hours of irradiation. This spectrum is displayed in Fig. 1(d). The line shown in Fig. 1(d) is similar to the spectrum of the S' center that is discussed in an earlier paper;[4] hence, the notation of S' center will be retained. Of the three main spectra shown in Fig. 1, the S' spectrum has been studied most extensively. The exact shape of the spectrum depends on the length of time that the sample was degassed at the elevated temperature, and on the length of time that the sample was irradiated. The latter dependence may be noted by comparing the curves in Fig. 2. The change of shape with the duration of irradiation indicates that the spectrum is really the spectra of two or more centers, each

growing at a different rate. Upon sufficient amplification of the S' center a set of six hyperfine lines could be detected (Fig. 3). The sum of the spins in the hyperfine spectrum becomes as great as 10% of the central line; the percentage is a function of the degassing and irradiation procedure. The maximum concentration of S' centers is equal to approximately 1% of the oxygen ions in the surface.

All three of these centers, the S_1, S_2, and S', could be saturated easily with microwave power at room temperature. Furthermore, all of the centers were rapidly and irreversibly destroyed by oxygen.

Samples of the purer MgO I were studied under the same conditions as the MgO II samples. The spectrum of the S_2 center was almost identical for the two samples. A spectrum much like that of S_1 center was observed in the unirradiated sample of MgO I that was degassed at 400° C. The intensity of the spectrum was increased by ultraviolet irradiation, and exposure to oxygen only destroyed this enhanced portion. The spectrum, after degassing at temperatures of 800° C and higher, was about the same as for the MgO II samples, but the intensity was somewhat less.

In an attempt to study the effects of doping, samples were used which also contained $Fe(NO_3)_3$, $AlCl_3$, or LiOH. The ferric nitrate samples were doped to an iron content of 0.005%, and were heated to 850° C for 16 hours. The S' spectrum was identical to that of the doped with $FeCl_3$. Aluminum choride also induced an enhanced S' spectrum. Samples doped with lithium (a monovalent impurity) exhibited,

when irradiated, the spectrum shown in Fig. 4, which differs considerably from the spectrum of the S' center. This lithium-affected center grew quite rapidly with irradiation, was easily saturated with microwave power, had a g value of 2.0009, and reacted rapidly with oxygen. This center will be referred to as an S center because of its similarity to the S center of Nelson and Tench.[2] The shape of the spectrum at first suggests uniaxial symmetry; however, a closer comparison of the spectrum with the calculated curves of Lebedev[7] indicates that the spectrum may be the result of a distribution of unequivalent lattice positions which cause, in turn, a distribution of g values.

Surface area measurements by the B.E.T. method indicate that the surfaces of the samples are continually changing, as shown in Fig. 5. The general shapes of the MgO I and MgO II curves of surface area versus temperature are similar, but the absolute values were not very reproducible. Some investigators have carried out much work on the surface area of MgO produced from $Mg(OH)_2$.[8,9] The scatter in the absolute areas is probably the result of differences in the partial pressure of water vapor during the degassing at 300° C.[8] It is interesting to note from the study of Kotera et al[9] that the growth rate of MgO crystals as a function of time and temperature can be divided into three groups. These groups roughly correspond to the degassing conditions at which the S_1, S_2, and S' centers were formed. Surface diffusion may be facilitated by the same defects that trap electrons to form the paramagnetic centers.

DISCUSSION

A definitive analysis of each of the centers described here is not possible at this time; however, it is worthwhile to propose some tentative models for the defects.

All of the irradiation-induced centers appear to be on the surface, since they react so readily with oxygen. Furthermore, the evidence suggests that the S_2, S', and S centers are electrons trapped at surface defects. This evidence includes the long relaxation time, g values less than 2.0023, and the hyperfine lines for the S' center. These hyperfine lines are the result of the mixing of the wave function of the unpaired electron with the orbitals on Mg^{25} nuclei. The hyperfine lines are apparently not observed for the other centers because of anisotropic interactions which result in line broadening. The characteristics of these three surface centers are all evident in F-type centers found in neutron-irradiated magnesium oxide single crystals.

The axial symmetry of the S_2 center indicates a simple defect such as an oxygen ion vacancy on the surface with a trapped electron. The expected g values would then be[10]

$$g_{\parallel} = 2, \; g_{\perp} = 2 - 2\frac{\lambda}{\delta} \tag{1}$$

where λ is the spin-orbit coupling constant and is positive. The term δ is the splitting between the s and p energy levels. The S_2 (600° C) center being on the surface (with no Mg^{+2} ion over it) accounts for the axial symmetry and allows the electron to have greater p-character. When bulk defects are considered, $g_{\parallel} > g_{\perp}$ is characteristic of an F_2 type center. The values of the present investigation

are in accord with $g_{||} = 2.0012$ and $g_{\perp} = 1.9998$.

The S center, which is formed in the lithium doped samples, also appears to be an electron trapped at a simple defect. Monovalent Li^+ would require a charge compensation center such as an oxygen ion vacancy. This oxygen vacancy, when irradiated, would then be capable of trapping an electron. A distribution of unequivalent lattice sites, as suggested by the shape of the curve, might be the result of lithium ions situated at varying distances from the oxygen vacancy.

Since trivalent impurities play a role in the formation of magnesium ion vacancies[3], and since the iron appears to have an effect on the concentration of S' centers, it seems reasonable to conclude that these cation vacancies combine with anion vacancies to form a surface defect that is similar to the bulk F_2 center.[10] The axis of this vacancy pair might lie either in the plane of the surface or perpendicular to the plane of the surface. In fact, both situations probably exist simultaneously. Partial annealing of the S' center at 150° C results in a spectrum that is quite similar to the S_2-center spectrum. This result indicates that an electron trapped at an oxygen ion vacancy contributes to the spectrum of Figs. 1(d) and 2. The identification of the S_1 center is somewhat more difficult, since the g values are appreciably greater than 2.0023. A center with $g_{\perp} = 2.011$ and $g_{||} = 2.0036$ was observed[11] in neutron irradiated BeO and was tentatively identified as an F center. The MgO samples that were heated to 300° C probably contained some regions which were still in the transition from the hydroxide hexagonal structure to the oxide face centered cubic structure. The unstable lattice could certainly contain a variety of defects.

Results of the present investigation indicate that several different defects exist on the surface of high-surface-area magnesium oxide. The nature of these defects varies with the degassing temperature and with altervalent ion impurities. Under certain conditions it is possible to obtain only one type of an observable center, while at other conditions several types of defects exist simultaneously.

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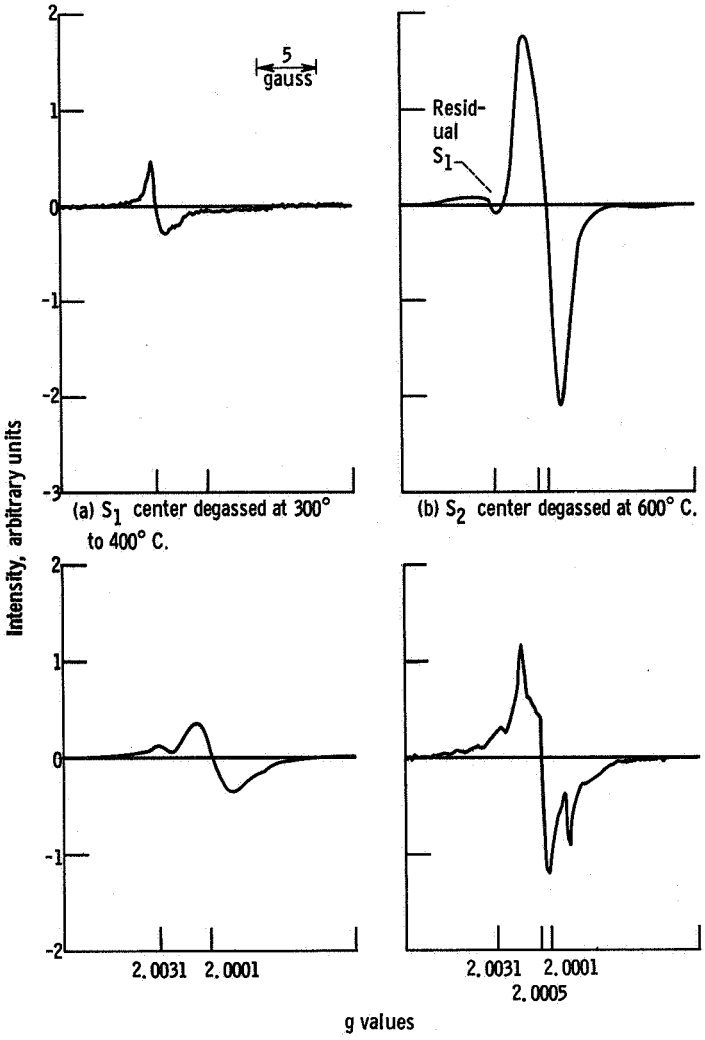

Figure 1. - Electron paramagnetic resonance derivative spectra of magnesium oxide sample II degassed 2 hours at the indicated temperature and irradiated with ultraviolet light for 24 hours.

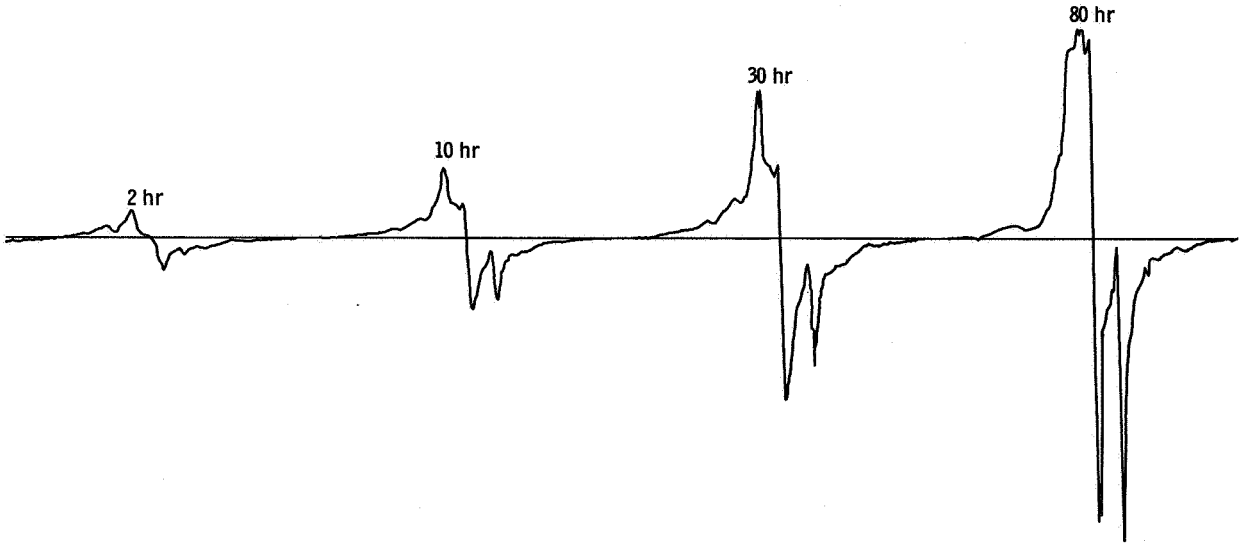

Figure 2. - Electron paramagnetic resonance derivative spectra of magnesium oxide sample II degassed for 20 hours at 850° C and irradiated for the indicated time. (S' center.)

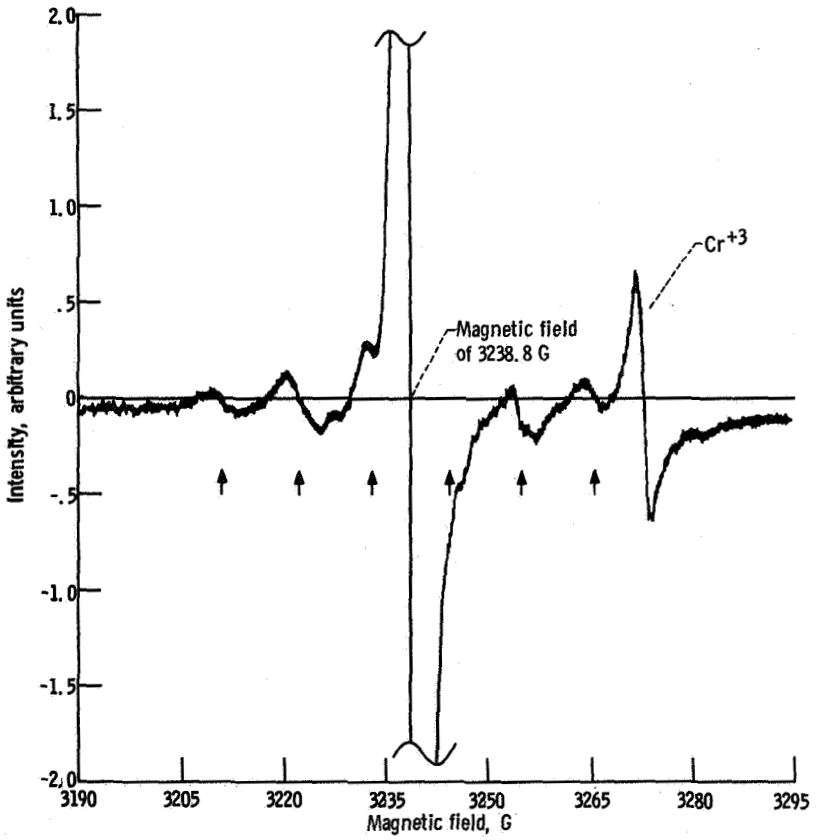

Figure 3. - Hyperfine lines (↑) for magnesium oxide sample II degassed 24 hours at 850° C and irradiated for 140 hours. (S' center.)

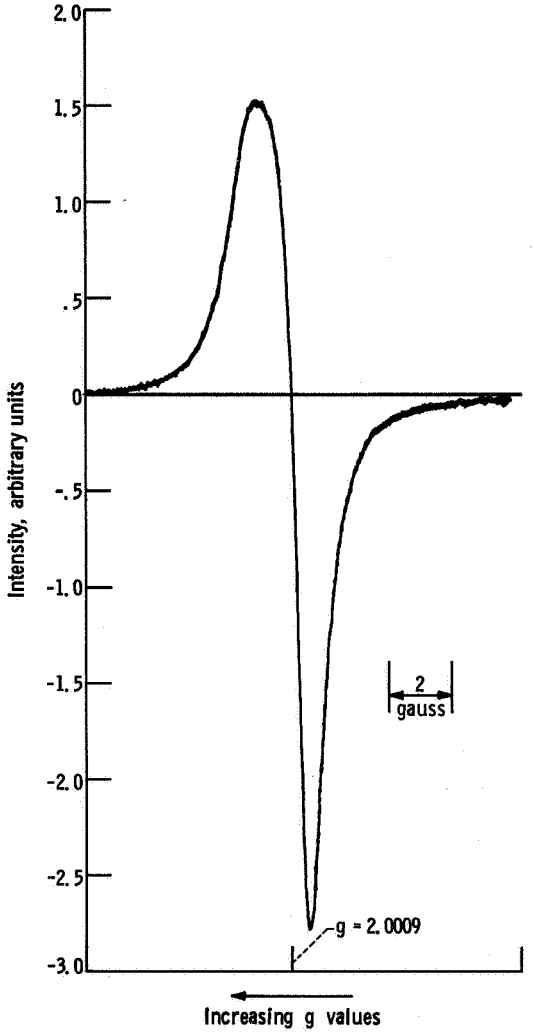

Figure 4. - Electron paramagnetic resonance derivative spectrum of lithium cation doped magnesium oxide degassed at 850° C and irradiated for 20 hours. (S center.)

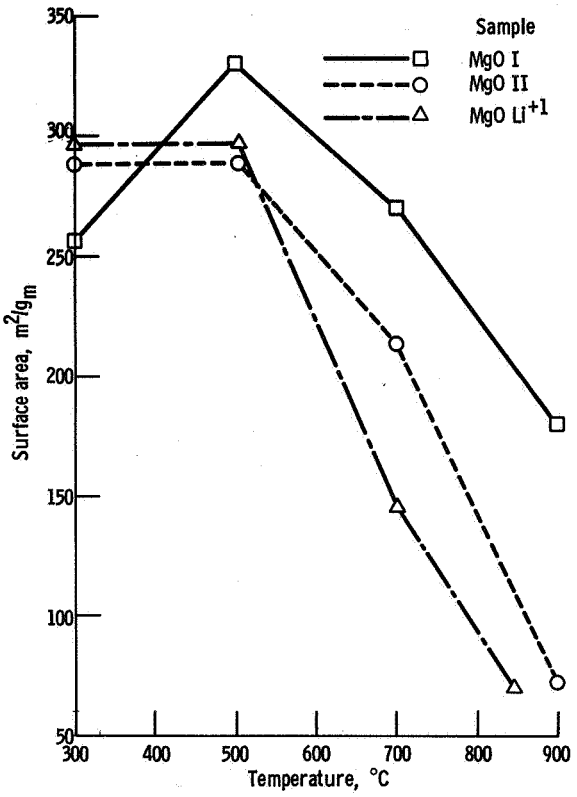

Figure 5. - Surface area of magnesium oxide samples as function of degassing temperature.